

# A Theoretical Study of Bond Energies in Model Si–H–Cl Molecules Using Density Functional Approaches for Representing Si Surface Chemistry

RANDALL C. BOEHM,<sup>1</sup> JOEL D. KRESS,<sup>2</sup> RICHARD L. MARTIN,<sup>2</sup>  
P. JEFFREY HAY<sup>2</sup>

<sup>1</sup>*School of Natural Sciences, New Mexico Highlands University, Las Vegas, New Mexico 87701*

<sup>2</sup>*Theoretical Division, MS B268, Los Alamos National Laboratory, Los Alamos, New Mexico 87545*

*Received 4 February 1997; accepted 12 August 1997*

**ABSTRACT:** The reliability of density functional theory (DFT) methods for calculating Si–H, Si–Cl, and Si–Si bond energies is examined in reactions involving molecules and small clusters representing various surface sites appropriate for Si surface chemistry. Results are presented for systematic studies using a valence double-zeta polarization basis for both all-electron calculations and valence-electron calculations employing effective core potentials (ECPs). All-electron DFT results are comparable to much more demanding MP4, G2, and MC-SCF-CI calculations for computed bond energies. Whereas the use of ECPs introduces systematic energy differences of ca. 3–5 kcal/mol compared to AE results, depending on the type of bond involved, the use of ECPs for carrying out calculations on larger clusters is discussed where AE calculations become more computationally demanding. The convergence of Si bond energies as a function of replacing hydrogens with silyl groups is examined. In constructing models to describe etching processes involving Cl species on Si surfaces, the need for incorporating differences in thermochemistries for one-, two-, and three-coordinate Si surface sites is emphasized. Comparisons of semiempirical approaches for thermochemistries of Si-containing species find

*Correspondence to:* P. J. Hay; email: pjhay@lanl.gov

Contract/grant sponsor: U.S. Department of Energy and Semiconductor Research Corporation (CRADA grant)

Contract/grant sponsor: Associated Western Universities (through the Department of Energy)

these methods somewhat less reliable for obtaining reliable bond energies compared to computationally more demanding DFT and *ab initio* correlated models. © 1997 John Wiley & Sons, Inc. *J Comput Chem* 18: 2075–2085, 1997

**Keywords:** silicon; *ab initio*; density functional; molecular orbital calculations; effective core potentials; surface chemistry models

## Introduction

In this work we report systematic theoretical studies of the thermochemistries of H- and Cl-containing silicon species appropriate for surface chemistry processes using density functional theory. Our focus is primarily on the performance of this method, as described by the Becke–Lee–Yang–Parr (BLYP) gradient-corrected exchange-correlation functional,<sup>1</sup> in predicting Si–H, S–Cl, and Si–Si bond energies in gas-phase Si species as well as in simple models for Si surface sites. We examine bond energies, their variation with coordination about the Si, and the convergence of the calculated properties with additional Si atoms in the model compounds. In addition, the use of effective core potentials (ECPs) in density functional calculations will be examined, because ECPs offer a means of reducing the overall computational expense, and hence, of treating larger clusters in modeling this chemistry.

The structures, thermochemistries and reactions of molecular H- and Cl-containing silicon species have been studied by a variety of *ab initio* theoretical methods in recent years including Moller–Plesset perturbation theory through MP4 level,<sup>2–5</sup> G2 level,<sup>6</sup> bond-additivity-corrected MP4,<sup>2,3</sup> coupled-cluster,<sup>7</sup> and MC–SCF–CI approaches.<sup>8</sup> In addition, the semiempirical MNDO(d) approach<sup>9</sup> has been developed and applied to Si- and Cl-containing compounds. Recently, we reported results of density functional calculations on simple Si–H–Cl species.<sup>10</sup>

The chemistry of silicon surfaces reacting with hydrogen and with halogens has remained an important technological area. The adsorption and desorption of hydrogen from silicon represent key processes in the formation of Si surfaces using chemical vapor deposition techniques in the semiconductor industry.<sup>11–13</sup> Similarly, the etching of Si surfaces<sup>14,15</sup> using  $\text{Cl}^+$  and  $\text{Cl}_2^+$  ions is widely used in the patterning of Si wafers for semiconductor applications.

Numerous theoretical studies have employed cluster models, typically with many more atoms in the cluster than employed here, to address thermochemical and kinetic issues associated with adsorption and desorption of hydrogen<sup>16–19</sup> and halogen<sup>20,21</sup> atoms and molecules. The alternative approach to such surface chemistry problems has been to employ band structure approaches for periodic arrays of atoms and, until recently, most band structure calculations employed the local density approximation (LDA)<sup>20–26</sup> in density functional theory. LDA has been shown to provide reasonable geometries for bulk and surface problems, but it typically overestimates chemical binding energies. Application of gradient corrections (LDA-GC)<sup>25–28</sup> have been shown to improve the results in cases reported to date.

## Computational Details

The density functional calculations were performed within the spin restricted formalism using the gradient-corrected Becke–Lee–Yang–Parr functional,<sup>1</sup> as implemented in the GAUSSIAN-94 or GAUSSIAN-92/DFT program suite.<sup>29</sup> The standard 6-31G\*\* basis was employed for all electron calculations. For valence-only calculations, the LANL2DZ basis with Si-effective core potential (ECP)<sup>30</sup> was augmented by the same polarization functions that are added to the 6-31G basis to construct the 6-31G\*\* basis. The semiempirical results reported in this article were generated by GAUSSIAN-94 for the AM1<sup>31</sup> and pM3<sup>32</sup> methods, or by SPARTAN 3.1<sup>34</sup> for the MNDO(d)<sup>9</sup> methods. Some minor differences were found for calculated heats of formation using SPARTAN 3.1 compared with the published results in ref. 9.

In the following section, the results of density functional calculations will be compared with experiment and with other theoretical approaches including both first principles methods and semiempirical methods. To compare with experiment, zero-point energies have been removed from the experimental heats of formation, as described in the Appendix. In the case of semiempirical

results, which are parameterized to heats of formation at 298 K, comparisons are made directly with experimental thermochemical enthalpies at 298 K.

### Comparison of Methods for Calculating Si—H and Si—Cl Bond Energies

In Tables I and II the results of various theoretical methods for abstracting a H or Cl atom, respectively, from molecules containing a single Si atom are compared using the BLYP density functional method in all-electron calculations (BLYP/AE) and employing effective core potentials (BLYP/ECP). In this section we focus on comparing these results with first principles MP4/AE results of Ho et al.<sup>2</sup> or G2 results of Su and Schlegel,<sup>28</sup> as well as with experiment.<sup>34–41</sup> As discussed in the Appendix, the experimental heats of formation have been corrected to account for both thermal and zero-point energies to compare with the calculated Si—H and Si—Cl bond energies. Because G2 results include zero-point energies, the quantities in Tables I and II are also corrected to remove zero-point effects to make all of the theoretical results directly comparable.

In an earlier work by one of the present investigators,<sup>10</sup> the BLYP and B3LYP density functional methods were found to give reasonably accurate

Si—H and Si—Cl bond energies in basis sets similar to the ones employed here. Typically, Si—H bond energies were underestimated by 1–2 kcal/mol, whereas Si—Cl bond energies were underestimated by 8–12 kcal/mol. These errors were typically half as large as the corresponding errors in MP4 calculations in the same basis set. Extensions to larger basis sets than 6-31G\*\* reduced the discrepancies by a few kilocalories per mole in the case of Si—Cl bonds.

The use of effective core potentials (ECP) in molecular density functional theory (DFT) calculations, as shown in the BLYP/ECP results in Tables I and II, has been investigated in recent years.<sup>42–44</sup> It has become a standard procedure to replace the inner core electrons by effective core potentials (ECP) in molecular Hartree–Fock calculations and by pseudopotentials in solid-state DFT band structure calculations. Although one might expect that an ECP appropriate for use in a specific DFT calculation should be based on the analogous atomic calculation, recent studies suggest that ECPs based on frozen-core Hartree–Fock calculations can give similar results to all-electron DFT calculations.<sup>43,44</sup>

The results in Table I show hydrogen abstraction energies for various Si—H bonds in molecules containing a single Si atom as calculated by all-electron density functional (BLYP/AE) and valence-electron density functional using effective

**TABLE I.** Si—H Bond Energies<sup>a</sup> From Density Functional and *Ab Initio* Calculations.<sup>b</sup>

Species	BLYP / ECP	BLYP / AE	MP4	G2	Experiment
SiH	76.9	74.1	65.9	73.8	72.0
SiH <sub>2</sub>	81.2	78.0	74.1	81.1	79.5
SiHCl	77.1	74.0	71.2	77.9	
SiH <sub>3</sub>	80.1	72.9	72.4	72.7	73.8
SiH <sub>2</sub> Cl	68.1	61.4	61.0	62.3	
SiHCl <sub>2</sub>	55.1	47.9	48.3	50.4	
SiH <sub>4</sub>	96.7	93.9	91.8	97.8	96.5
SiH <sub>3</sub> Cl	95.5	92.3	92.2	97.9	
SiH <sub>2</sub> Cl <sub>2</sub>	94.4	90.8	92.3	97.9	
SiHCl <sub>3</sub>	94.0	89.9	92.5	—	95.9
Avg. error	3.1	2.8	4.2	1.4	

<sup>a</sup> Si—H bond energies in Kilocalories per mole.

<sup>b</sup> All quantities refer to relative energies at 0 K without zero-point corrections. Experimental quantities have been corrected from measured values at 298 K (see Appendix).

**TABLE II.**  
**Si—Cl Bond Energies<sup>a</sup> From Density Functional and *Ab Initio* Calculations.<sup>b</sup>**

Species	BLYP / ECP	BLYP / AE	MP4 / AE	G2	Exp.
SiCl	98.4	98.8	87.4	100.4	99.1
SiHCl	98.6	98.7	92.8	104.5	
SiCl <sub>2</sub>	97.6	97.9	92.8	104.7	107.2
SiH <sub>2</sub> Cl	85.5	82.1	79.6	85.7	
SiHCl <sub>2</sub>	75.6	71.8	69.9	77.2	
SiCl <sub>3</sub>	61.9	57.4	57.0	—	69.6
SiH <sub>3</sub> Cl	101.0	101.4	99.3	110.9	112.9
SiH <sub>2</sub> Cl <sub>2</sub>	101.8	101.2	101.2	112.8	
SiHCl <sub>3</sub>	100.8	99.4	101.3	—	
SiCl <sub>4</sub>	98.4	96.0	100.1	—	107.4
Avg. error	7.8	8.9	11.9	1.7	

<sup>a</sup> Si—Cl bond energies in Kilocalories per mole.  
<sup>b</sup> All quantities refer to relative energies at 0 K without zero-point corrections. Experimental quantities have been corrected from measured values at 298 K (see Appendix).

core potentials (BLYP/ECP). Similar results are given in Table II for Si—Cl bonds. All-electron MP4 calculations of Ho et al.<sup>2</sup> in the same basis are also reported in the tables. The calculated bond energies typically increase MP4 < BLYP/AE < BLYP/ECP. For chlorine abstraction energies the BLYP/AE and MP4 calculations are in fairly close agreement, whereas BLYP/ECP calculations overestimate Si—Cl bond energies by 3–6 kcal/mol compared with the all-electron (BLYP/AE) results. In Tables I and II, the average unsigned errors between calculated and available experimental results are given along with the results of the computationally more demanding G2 approach by Su and Schlegel.<sup>5</sup> The errors (in kilocalories per mole) increase in the order G2 (1.4), BLYP/AE (2.8), BLYP/ECP (3.1), and MP4 (4.2) for Si—H bond energies and G2 (1.7), BLYP/ECP (7.8), BLYP/AE (8.9), and MP4 (11.9) for Si—Cl bond energies.

In Table III we report the calculated bond energies for semiempirical AM1,<sup>31</sup> PM3,<sup>32</sup> and MNDO(d)<sup>9</sup> methods. Because these methods are parameterized for heats of formation at 298 K we compare these results directly with bond *enthalpies* at 298 K using the measured heats of formation given in the Appendix. Although the performance is encouraging for many species, there exist many cases with significant discrepancies compared to the known thermochemical bond enthalpies. The best performance is given by the recently parameterized MNDO(d) method for which average er-

**TABLE III.**  
**Si—H and Si—Cl Bond Enthalpies at 298 K (kcal / mol) From Semiempirical Calculations and Corresponding Measured Quantities at 298 K (see Appendix).**

Species	AM1	PM3	MNDO(d)	Exp.
Si—H bond enthalpies				
SiH	71.0	65.9	71.2	69.8
SiH <sub>2</sub>	73.7	73.9	76.9	76.6
SiH <sub>3</sub>	95.4	81.9	70.4	69.6
SiH <sub>4</sub>	72.4	82.5	86.4	91.9
SiHCl <sub>3</sub>	58.9	69.9	73.4	90.6
Avg. error	16.2	9.8	5.0	
Si—Cl bond enthalpies				
SiCl	110.4	107.6	104.6	98.8
SiCl <sub>2</sub>	102.2	108.2	103.1	107.2
SiCl <sub>3</sub>	100.6	74.4	76.6	68.8
SiH <sub>3</sub> Cl	91.1	99.5	105.3	110.9
SiCl <sub>4</sub>	81.6	90.5	90.5	107.3
Avg. error	18.8	8.7	8.0	

rors are 5 and 8 kcal/mol for Si—H and Si—Cl bond enthalpies, respectively. A more extensive discussion of MNDO(d) applications to Si compounds is given by Thiel and Voityuk.<sup>9</sup> Semiempirical methods have been used for a number of studies pertaining to silicon surface chemistry,<sup>41</sup> including the determination of adatom bond energies, lengths, and frequencies. It is not

apparent that current parameterizations of semi-empirical methods are well suited for this purpose because there is a shortage of reliable, directly measured heats of formation of small silicon-containing molecules. Such data are required to arrive at the parameters used in such methods for the relatively simple algebraic formulas that replace the one-electron and two-electron integrals.

### Substituent and Coordination Effects on Bond Energies

In this section, the effects of substituents on Si—H, Si—Cl, and Si—Si bonds are examined using DFT results given in Tables IV, V, and VI, respectively. The changes in bond energies when neighboring hydrogens are replaced by silyl (SiH<sub>3</sub>—denoted *Si* in the tables) and longer chain silicon substituents are examined to assess the use of small clusters to calculate silicon surface thermochemistries. Also, the effects of replacing hydrogens by more electronegative chlorine atoms are discussed. Finally, the differences in coordination about the Si are found to play an important role in the overall thermochemistries as well as in the ability of ECP calculations to mimic the results of all electron calculations. In two-coordinate SiX<sub>2</sub>

and SiX compounds, one is forming bonds with an orbital on the Si that is essentially 3p-like in character, because the local electronic structure is essentially (3s)<sup>2</sup>(3p)<sup>2</sup>, whereas, in four-coordinate SiX<sub>4</sub> and SiX<sub>3</sub> compounds, the bonding is more sp<sup>3</sup> in character, by contrast. This is most transparent in the respective geometries, as observed by the nearly 90° bond angles in SiX<sub>2</sub> compounds and nearly tetrahedral X—Si—X angles in three- and four-coordinate silicon compounds.

Tables III–V the current all-electron (BLYP/AE) and effective core potential (BLYP/ECP) results are presented for Si—H, Si—Cl, and Si—Si bond energies. Also presented are the MC-SCF-CI results of Sax and Kalcher.<sup>8</sup> These bond energies correspond to the dissociation energy, *D<sub>e</sub>*, without zero-point corrections and at 0 K.

As will be discussed in greater detail, with regard to the comparison of the BLYP results (either AE or ECP) with experiment, overall, the performance is quite satisfactory for Si—H bonds within 1–2 kcal/mol of experiment, whereas Si—Cl bonds are underestimated by 10–12 kcal/mol in the modest polarized valence double-zeta basis. In silane compounds, the Si—Si bond energies agree quite well with experiment, whereas, for chlorosilane compounds, these Si—Si energies are underestimated by as much as 15

**TABLE IV.**  
Comparison of Calculated and Corrected Experimental Si—H Bond Energies at 0 K (see Appendix).  
Experimental Bond Enthalpies at 298 K Also Given.

Type of bond ( <i>Si</i> denotes SiH <sub>3</sub> )	Bond energy (kcal / mol) at 0 K			Bond enthalpy (kcal / mol) at 298 K in exp.
	BLYP / AE	BLYP / ECP	Exp.	
<i>Four-coordinate species</i>				
H—SiH <sub>3</sub>	93.9	96.7	96.5	91.9
—SiH <sub>2</sub> <i>Si</i>	90.0	93.8	—	
—SiHSi <sub>2</sub>	—	91.0	—	
—SiSi <sub>3</sub>	—	88.6	—	
<i>Two-coordinate species</i>				
H—SiH	78.0	81.2	79.5	76.6
—SiCl	74.0	77.1	—	
—SiSi	77.2	80.1	—	
<i>Three-coordinate species</i>				
H—SiH <sub>2</sub>	73.0	80.1	73.8	69.6
—SiHCl	61.4	68.1	—	
—SiCl <sub>2</sub>	47.9	55.1	—	
—SiHSi	73.7	81.0	—	

**TABLE V.** Comparison of Calculated and Corrected Experimental Si—Cl Bond Energies at 0 K (see Appendix). Experimental Bond Enthalpies at 298 K Also Given.

Type of bond ( <i>Si</i> denotes SiH <sub>3</sub> )	Bond energy (kcal / mol) at 0 K			Bond enthalpy (kcal / mol) at 298 K in exp.
	BLYP / AE	BLYP / ECP	Exp.	
<i>Four-coordinate species</i>				
Cl—SiH <sub>3</sub>	101.4	101.0	109.0	114.8
—SiH <sub>2</sub> <i>Si</i>	—	97.9	—	
—SiH <i>Si</i> <sub>2</sub>	—	94.4	—	
—Si <i>Si</i> <sub>3</sub>	—	92.0	—	
—Si <sub>3</sub> H <sub>7</sub>	—	97.4	—	
Cl—SiCl <sub>3</sub>	96.0	98.4	110.9	108.1
—SiCl <sub>2</sub> —SiH <sub>3</sub>	96.1	98.1	—	
—SiCl <sub>2</sub> —SiCl <sub>3</sub>	95.0	—		110.1
—SiCl <sub>2</sub> — <i>Si</i> <sub>3</sub>	97.3			
<i>Two-coordinate species</i>				
Cl—SiH	98.7	98.6	—	
—SiCl	97.9	97.6	107.2	107.2
—Si <i>Si</i>	95.9	95.4	—	
<i>Three-coordinate species</i>				
Cl—SiH <sub>2</sub>	82.1	85.5		
—SiHCl	71.8	75.6		
—SiCl <sub>2</sub>	57.4	61.9	69.6	68.8
—SiCl— <i>Si</i>	75.9	79.6	—	
—SiCl—Si <i>Si</i> <sub>3</sub>	—	77.9	—	

kcal/mol by the BLYP calculations in the 6-31G\*\* basis sets employed here. Although much larger basis sets could be employed for the smaller molecules being considered, such basis sets are a compromise between accuracy and computational expense for performing calculations on more realistic clusters containing 10 or more silicon atoms.

One major issue addressed in Tables IV–VI is the dependence of computed bond energies on the environment about the specific bond in question. Starting with four-coordinate systems, in X<sub>3</sub>Si—H molecules the Si—H bond weakens steadily from 97 to 89 kcal/mol as saturating hydrogen atoms are replaced with silyl groups (Si), as shown in Table IV, and very slightly—from 97 to 94 kcal/mol—as they are replaced with chlorine atoms (Table I). For Si—Cl bonds of the form X<sub>3</sub>Si—Cl, the bond energy steadily decreases from 101 kcal/mol for H<sub>3</sub>Si—Cl to 92 kcal/mol for Si<sub>3</sub>Si—Cl as shown in Table V. As saturating hydrogens are replaced with chlorine atoms (Table II), the bond energies decrease from 101 to 96 kcal/mol in going from SiH<sub>3</sub>Cl to SiCl<sub>4</sub>. Extend-

ing the silyl chain from Cl—Si<sub>2</sub>H<sub>5</sub> (i.e., Cl—SiH<sub>2</sub>Si) to Cl—Si<sub>3</sub>H<sub>7</sub> has no effect on the Si—Cl bond.

In two-coordinate XSi—H systems, the Si—H bond energies vary with X as H ≈ SiH<sub>3</sub> > Cl, with the first two being stronger by 3–4 kcal/mol. For Si—Cl bonds in X—Si—Cl species, the variation is H ≈ Cl > SiH<sub>3</sub>, with the first two again stronger by about 3 kcal/mol.

For Si—Si bonds, little difference is observed in going from Si<sub>2</sub>H<sub>6</sub> (73 kcal/mol) to Si<sub>3</sub>H<sub>8</sub> (71 kcal/mol) or in going from Si<sub>2</sub>H<sub>6</sub> to Si<sub>2</sub>Cl<sub>6</sub> (Table VI). When all hydrogens are replaced by silyl groups in Si<sub>3</sub>Si—SiSi<sub>3</sub>, however, the resultant strain reduces the bond energy to 60 kcal/mol, somewhat closer to the average bond energy of 53 kcal/mol in bulk silicon.<sup>46</sup> For Cl<sub>3</sub>Si—SiX<sub>3</sub> systems, the bond energy decreases from 71 to 66 kcal/mol, as hydrogens are replaced by silyl groups. Similarly, for ClSi—SiX<sub>3</sub> molecules, a similar decrease is found as hydrogens are replaced by Si.

**TABLE VI.**  
**Comparison of Calculated and Corrected Experimental Si—Si Bond Energies at 0 K (see Appendix).**  
**Experimental Bond Enthalpies at 298 K also Given.**

Type of bond (Si denotes SiH <sub>3</sub> )	Bond energy (kcal / mol) at 0 K				Bond enthalpy (kcal / mol) at 298 K in exp.
	BLYP / AE	BLYP / ECP	MC –SCF –CI	Exp.	
<i>Four-coordinate Si</i>					
SiH <sub>3</sub> —SiH <sub>3</sub>	72.2	72.9	76.5	79.8	73.6
—Si <sub>2</sub> H <sub>5</sub>	—	71.1	72.1	83.2	72.4
—SiH <sub>2</sub> Cl	—	71.6	—		
—SiHCl <sub>2</sub>	—	70.8	—		
—SiCl <sub>3</sub>	—	71.4	—		
SiCl <sub>3</sub> —SiH <sub>3</sub>	—	71.4	—		
—Si <sub>2</sub> H <sub>5</sub>	—	69.9	—		
—Si <sub>3</sub> H <sub>7</sub>	—	69.1	—		
—SiHSi <sub>2</sub>	—	68.1	—		
—SiSi <sub>3</sub>	—	66.3	—		
—SiCl <sub>3</sub>	62.5	66.5	—		68.7
Si <sub>3</sub> Si—SiSi <sub>3</sub>	—	59.8	—		
<i>Two-Coordinate Si</i>					
SiH—SiH <sub>3</sub>	58.6	59.4	59.4	59.5	57.6
SiCl—SiH <sub>3</sub>	52.6	53.1	—		
—Si <sub>2</sub> H <sub>5</sub>	—	52.8	—		
—Si <sub>3</sub> H <sub>7</sub>	—	52.4	—		
—SiHSi <sub>2</sub>	—	51.4	—		
—SiSi <sub>3</sub>	—	50.6			
<i>Three-Coordinate Si</i>					
SiH <sub>2</sub> —SiH <sub>3</sub>	54.3	59.2	57.2	63.3	58.3
—Si <sub>2</sub> H <sub>5</sub>	—	58.1	56.0		
SiCl <sub>2</sub> —SiH <sub>3</sub>	30.7	35.2	—		
—SiSi <sub>3</sub>	—	30.9	—		

The BLYP/ECP calculations generally mimic the all-electron results for the aforementioned molecules, but overestimate four-coordinate Si—Cl bonds by 2 kcal/mol and two- and three-coordinate Si—H bonds by 3 kcal/mol. In the limited number of comparisons made in Table VI, ECP calculations give good agreement with all-electron results for Si(sp<sup>3</sup>)—Si(sp<sup>3</sup>) and Si(sp<sup>3</sup>)—Si(p) bonds. Similar discrepancies between ECP and all-electron results have been noted previously by Nachtigal et al.<sup>18c</sup> in studies of Si clusters. They found that the use of pseudopotentials in calculations of reaction energies and barriers led to discrepancies when compared with all-electron calculations using the same 6-311G(d,p) basis set, of 2–4 kcal/mol at the LSD level, 3–8 kcal/mol for BLYP, and 2–10 kcal/mol for MP4(SDQ).

In Tables IV–VI we have listed bond energies for reactions involving three-coordinate Si yielding products with two-coordinate Si. In the pattern of Si—Cl bond energies as successive chlorine atoms are removed from SiCl<sub>4</sub> (108 kcal/mol experimentally), SiCl<sub>3</sub> (69.5), SiCl<sub>2</sub> (111), and SiCl (94.6), the large change for SiCl<sub>3</sub> arises from the fact that the promotion energy from 3s<sup>2</sup>3p<sup>2</sup> to 3s<sup>1</sup>3p<sup>3</sup> is involved as Cl leaves to form SiCl<sub>2</sub>.

In atomic spectroscopic language, silicon is in the <sup>3</sup>P state when it is one or two coordinate and in the <sup>5</sup>S state when it is three or four coordinates. As shown in Table VII, the atomic excitation energy (Δ*E*<sub>ex</sub>) is 95 kcal/mol experimentally,<sup>43</sup> but this quantity is overestimated (106 kcal/mol) using BLYP whereas Hartree–Fock underestimates this excitation energy substantially (57 kcal/mol).

**TABLE VII.**  
**Calculated and Experimental Si 3s<sup>2</sup>3p<sup>2</sup> (<sup>3</sup>P)—3s3p<sup>3</sup> (<sup>5</sup>S) Promotion Energies. Theoretical Results Obtained Using 6-31G Basis.**

Method	$E(^5\text{S}) - E(^3\text{P})$ kcal/mol	
	AE	ECP
Hartree-Fock	57.3	48.1
BLYP	106.6	93.8
Exp. <sup>a</sup>		95

<sup>a</sup> Ref. 47

in the all-electron 6-31G\*\* basis. ECP calculations tend to give corresponding lower values than the all-electron counterpart for both HF (48 kcal/mol) and BLYP (94 kcal/mol) calculations—about 12% lower in each case.

The bond energy for three-coordinate Si compounds ( $E_{b3}$ ) should be approximately:

$$E_{b3} \approx E_{b4} - \Delta E_{\text{ex}}$$

that is, the normal four-coordinate bond energy,  $E_{b4}$ , minus the atomic excitation energy. Because,  $\Delta E_{\text{ex}}$  is underestimated in BLYP/ECP, compared with BLYP/AE (as well as HF/ECP compared to HF/AE), we therefore expect the BLYP/ECP bond energies to be higher than the corresponding BLYP/AE values in these systems. Indeed, examination of the three-coordinate Si compounds in Tables I and II shows much greater discrepancies between AE and ECP results—about 8 kcal/mol for Si—H bond energies and 4 kcal/mol for Si—Cl bond energies—than found for either four-coordinate or two-coordinate species. Similar effects are found in Tables III–V where the bond involves a change from three- to two-coordinate species.

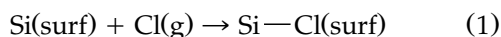
As far as substituent trends are concerned, one sees a marked decrease (Table IV) in H—SiX<sub>2</sub> bond energy, as as hydrogens are replaced by Cl in the SiX<sub>2</sub> species, from 80 to 55 kcal/mol. Similarly, for Cl—SiX<sub>2</sub> species, a steady decrease from 85 to 62 kcal/mol is found as hydrogens are replaced by Cl atoms.

## Clusters as Models for Surface Sites for Cl Etching

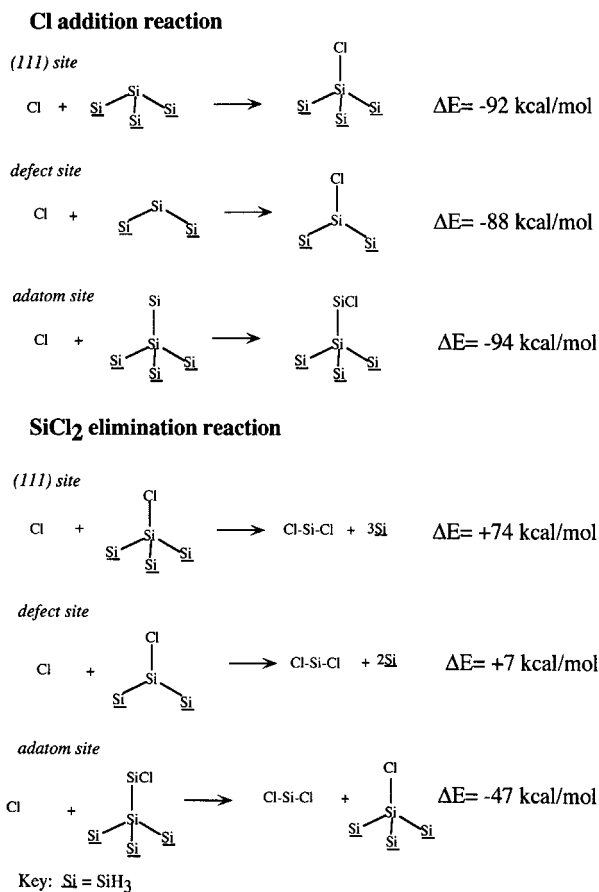
The preceding discussion has shown that cluster models with at least the first coordination shell about the surface atom site should be capable of providing information about thermochemistries of adsorbates on Si using density functional theory.

Also, the calculations have shown that the Si bond energy is influenced by the local coordination and hybridization of the orbitals involved in the bonding. In this section, we illustrate briefly these effects for Si—Cl bond-breaking processes that would occur in simulations of these processes.

For an etching process, the Si surface is continually bombarded by Cl ions, which react with the Si atoms to form Si—Cl bonds. These species in turn react with other Cl species, which eventually results in evolution of silicon-containing species, most notably SiCl<sub>2</sub>, from the surface. These processes are illustrated by two reactions shown in Figure 1. In the first type of reaction unsaturated Si atoms are shown to react with neutral Cl atoms, after neutralization of the incident positive ions, to form Si—Cl surface species (adsorption):



The nature of the Si(surf) species is crucial to the chemistry, and these species could be one of at



**FIGURE 1.** Representative surface Si/Cl reactions.

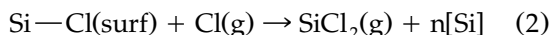


least three distinct types:

- A (111) Si site, where there are three bonds to neighboring atoms and a single unpaired electron on the site.
- A defect site, where there are two bonds to neighboring atoms and two electrons in a nonbonding lone pair on the site.
- An adatom site, where there is a single bond to atoms below on the surface and three nonbonding electrons (a lone pair and one unpaired electron) reside on the site.

The resultant thermochemistries arising from Cl-bond formation to these three sites varies, not surprisingly in view of the preceding discussion. Bonding to the (111) site involves an four-coordinate species, to the defect site involves a three-coordinate species, and to the adatom site involves a two-coordinate species. The overall result is that the energies for the reactions are  $-94$ ,  $-88$ , and  $-92$  kcal/mol, respectively.

A subsequent process is shown in the second part of Figure 1, where these Si—Cl bonds react with Cl to form SiCl<sub>2</sub> (etching):



where [Si] represents possible other Si sites generated after SiCl<sub>2</sub> is evolved. These three possibilities are given in the figure where the overall thermochemistries now are  $-47$ ,  $+7$ , and  $+74$  kcal/mol for (111), defect, and adatom sites, respectively. These energies vary more widely in this situation because of the differences in Si—Si bonds that are broken during the various processes.

The previous example shows that simulations of surface processes such as etching and deposition should include thermochemistries that are both reasonably accurate, as given by density functional theory in the present case, as well as sufficiently flexible to describe the various bonding states and coordinations that will occur in these processes.

## Conclusions

The energy of Si—H, Si—Cl and Si—Si bonds in model compounds that represent the types of bonding situations encountered on Si surfaces have been systematically examined using density functional theory. In addition, the use of effective core potentials in density functional calculations has

also been explored. The use of an effective core potential usually leads to somewhat stronger Si—X bonds, where the difference is most pronounced in reactions of SiX<sub>3</sub> going to SiX<sub>2</sub>. In other types of reactions, the difference between the AE and ECP results is quite systematic which suggests that any errors can be estimated fairly consistently. The effect of using ECP instead of AE results is to add systematically 1.0–1.5 kcal/mol to Si—H bond energies, 3.4–4.4 kcal/mol to Si—Cl bond energies, and approximately 2 kcal/mol to the energy of Si—Si bonds on the basis of a smaller set of comparisons. These small but significant differences arising from the use of ECPs appear to be acceptable for surveying silicon chemistry in view of the overall good performance of density functional theory in predicting thermochemistries compared to Hartree–Fock or the much more computationally intensive MP4 calculations. One would expect relative reaction energies to be even more reliable.

Of the semiempirical methods examined here, the AM1 and PM3 methods predicted bond enthalpies in error by 10–20 kcal/mol for reactions involving small silicon molecules. The recently parameterized MNDO(d) method gave the best performance with average errors of only 5 and 8 kcal/mol for Si—H and Si—Cl bond enthalpies, respectively.

The chemical results can be divided into three families of reactions:

- SiX<sub>4</sub> → SiX<sub>3</sub> + X
- SiX<sub>3</sub> → SiX<sub>2</sub> + X
- SiX<sub>2</sub> → SiX + X and SiX → Si + X

In family A, the silicon to hydrogen bond energy is approximately 90 kcal/mol, the silicon to chlorine bond energy is approximately 100 kcal/mol, and the silicon to silicon bond energy is especially sensitive to the nature of the saturating groups, ranging from 60 to 70 kcal/mol. In family C, these three bond types are 75, 95, and 50 kcal/mol, respectively. The family B reaction energy predictions are less accurate, and the origin of the problem with these reactions may be traced to an overestimate of BLYP in predicting the <sup>5</sup>S to <sup>3</sup>P energy difference for a silicon atom.

Regarding the surface chemistry component, we observe that saturating silyl groups tend to decrease silicon to X bond strengths somewhat: in the first sphere, this effect ranges from 1.0 to 4.4 kcal/mol per group; and, in the second sphere,

this effect is approximately 0.5 kcal/mol per group (excluding family B in each case). The coordination number of the silicon is shown to be important with respect to bond energy, underscoring the need to use site-specific silicon potentials in future molecular dynamics simulations of Cl etching of Si surfaces.

Appendix

The calculated bond energies in this study have been compared with experimental values based on available thermochemical properties.<sup>33–41</sup> In this article, the starting point is the standard heats of formation at 298 K for the Si-containing species given in Table VIII. Standard values for the more stable species are typically taken from the thermochemical compilations in the JANAF or CATCH tables. Other recent experimentally determined values for the more reactive species are cited specifically in the table. The cases of SiCl and SiCl<sub>3</sub> have been controversial, where there has been considerable divergence among experimental values as well as with the results of highly accurate theo-

retical calculations. The value for SiCl<sub>3</sub> here is taken from the earlier experiments of Walsh and Wells,<sup>37</sup> whereas the value for SiCl comes from the BAC-MP4 estimates of Ho et al.<sup>2</sup>

The bond enthalpies at 298 K in Tables IV–VI correspond simply to the differences in heats of formation,  $\Delta H_{f298}$ , between products (P) and reactants (R):

bond enthalpy =  $\Delta H_{f298}(P) - \Delta H_{f298}(R)$

or, equivalently, as the differences in the atomization enthalpies,  $\Delta H_a$ , corresponding to the reverse process of dissociating the molecules into their constituent atoms

bond enthalpy =  $\Delta H_a(R) - \Delta H_a(P)$

The calculated bond energies correspond to the energy differences at 0 K and without zero-point vibrational corrections

bond energy =  $\Delta E_a(R) - \Delta E_a(P)$

where  $\Delta E_a$  are now the atomization *energies*. These quantities are related as follows:

$$\Delta H_a = \Delta E_a - \text{ZPE} + \Delta H(\text{tr} + \text{rot} + \text{vib}) + \Delta(\text{PV})$$
$$= \Delta E_a - \Delta H_{\text{corr}}$$

where the atomization energy is corrected by the zero-point energy (ZPE) at 0 K, plus the contributions of translation, rotation, and vibration as well as PV work between 0 K and 298 K. The contribution to the atomization energy for finite temperature as well as zero-point energy,  $\Delta H_{\text{corr}}$ , have been taken from the calculations by Ho et al.<sup>2</sup> and by Sax and Kalcher<sup>8</sup> in their theoretical studies of silicon-containing species. These corrections, which are also given in Table VIII, have been used to correct experimental bond enthalpies to obtain experimental bond energies at 0 K analogous to the computed values.

TABLE VIII.  
Thermochemical Quantities for Si—H—Cl Compounds. Experimental Heats of Formation at 298 K and Theoretical Values for Zero-Point and Thermal Corrections to Enthalpies of Atomization at 298 K to Obtain Electronic Energies at 0 K.

Species	$\Delta H_f^{298}$ (kcal / mol)	Ref.	Zero-point and thermal correction	Ref.
SiH <sub>4</sub>	8.2	34	14.1	2a
SiH <sub>3</sub>	48.0	38	9.5	2a
SiH <sub>2</sub>	65.5	35	5.3	2a
SiH	90.0	34	2.2	2a
SiCl <sub>4</sub>	−158.4	34	1.2	2a
SiCl <sub>3</sub>	−80.1	37	1.1	2a
SiCl <sub>2</sub>	−40.3	34	0.3	2a
SiCl	37.9	2	0.3	2a
SiH <sub>3</sub> Cl	−33.9	34	11.5	2a
SiHCl <sub>3</sub>	−118.6	39	5.3	2a
Si <sub>2</sub> H <sub>6</sub>	19.1	39	22.0	2b
Si <sub>2</sub> H <sub>5</sub>	53.3	41	17.7	8
SiH—SiH <sub>3</sub>	74.7	36	13.6	2b
Si <sub>3</sub> H <sub>8</sub>	28.9	39	30.2	8
Si <sub>2</sub> Cl <sub>6</sub>	−228.9	40		
H	52.103	34		
Cl	28.989	34		
Si	107.7	34		

References

1. C. Lee, W. Yang, and R. G. Parr, *Phys. Rev. B*, **37**, 785 (1988); A. D. Becke, *Phys. Rev. A*, **38**, 3098 (1988).  
2. (a) P. Ho, M. E. Coltrin, J. S. Binkley, and C. F. Melius, *J. Phys. Chem.*, **89**, 4647 (1985); (b) *J. Phys. Chem.*, **90**, 3393 (1986).  
3. M. D. Allendorf and C. F. Melius, *J. Phys. Chem.*, **97**, 720 (1993).  
4. M. S. Gordon, T. N. Truong, and E. K. Bonderson, *J. Am. Chem. Soc.*, **108**, 1421 (1986).

5. M.-D. Su and H. B. Schlegel, *J. Phys. Chem.*, **97**, 8732 (1993).
6. C. C. Darling and H. B. Schlegel, *J. Chem. Phys.*, **97**, 8207 (1993).
7. R. Grev and H. F. Schaefer III, *J. Chem. Phys.*, **97**, 8389 (1992).
8. A. F. Sax and J. Kalcher, *J. Phys. Chem.*, **95**, 1768 (1991).
9. W. Thiel and A. A. Voityuk, *J. Mol. Struct. (Theochem)*, **313**, 141 (1984).
10. P. J. Hay, *J. Phys. Chem.*, **100**, 5 (1996).
11. M. L. Hitchman and K. F. Jensen, In *Chemical Vapor Deposition*, M. L. Hitchman and K. F. Jensen, Eds., Academic Press San Diego, CA, 1993, p. 159.
12. J. M. Jasinski, R. Becerra, and R. Walsh, *Chem Rev.*, **95**, 1203 (1995).
13. H. N. Waltenburg and J. T. Yates, Jr., *Chem. Rev.*, **95**, 1589 (1995).
14. D. Manos and D. L. Flamm, *Plasma Etching: An Introduction*, Academic Press, Boston, 1989.
15. H. Winters and J. Coburn, *Surf. Sci. Rep.*, **14**, 163 (1992).
16. (a) A. Redondo, W. A. Goddard III, and T. C. McGill, *Phys. Rev.*, **B24**, 6135 (1981); (b) A. Redondo and W. A. Goddard, *J. Vac. Sci. Technol.*, **21**, 344 (1982).
17. (a) C. J. Wu, I. V. Ionova, and E. A. Carter, *Surf. Sci.*, **295**, 64 (1993); (b) *Phys. Rev. B*, **49**, 13488 (1994); (c) C. J. Wu and E. A. Carter, *Phys. Rev. B*, **46**, 4651 (1992); (d) *Chem. Phys. Lett.*, **185**, 172 (1991).
18. (a) P. Nachtigal, K. D. Jordan, and C. Sosa, *J. Chem. Phys.*, **101**, 8073 (1994); (b) *J. Phys. Chem.*, **97**, 11666 (1993); (c) P. Nachtigal, K. D. Jordan, A. Smith, and H. Jonsson, *J. Chem. Phys.*, **104**, 148 (1996).
19. Z. Jing and J. L. Whitten, *J. Chem. Phys.*, **98**, 7466 (1993).
20. (a) C. J. Wu and E. A. Carter, *J. Am. Chem. Soc.*, **113**, 9061 (1991); (b) C. J. Wu and E. A. Carter, *Phys. Rev.*, **B45**, 9065 (1992).
21. (a) B. J. Garrison and W. A. Goddard III, *J. Chem. Phys.*, **87**, 1307 (1987); (b) B. J. Garrison and W. A. Goddard III, *Phys. Rev. B*, **36**, 9805 (1987).
22. P. Kruger and J. Pollman, *Phys. Rev. B*, **47**, 1898 (1993).
23. G. W. Li, Y. C. Chang, R. Tsu, and J. E. Greene, *Surf. Sci.*, **330**, 20 (1995).
24. A. De Vita, I. Stich, M. J. Gillan, M. C. Payne and L. J. Clarke, *Phys. Rev. Lett.*, **71**, 1276 (1993).
25. E. Pehlke and M. Scheffler, *Phys. Rev. Lett.*, **74**, 952 (1995).
26. P. Kratzer, B. Hammer, and J. K. Nørskov, *Chem. Phys. Lett.*, **229**, 645 (1994).
27. A. Vittadini and A. Selloni, *Chem. Phys. Lett.*, **235**, 334 (1995).
28. A. P. Smith, J. K. Wiggs, H. Jonsson, H. Yan, L. R. Corrales, P. Nachtigal, and K. D. Jordan, *J. Chem. Phys.*, **102**, 1044 (1995).
29. M. J. Frisch, G. W. Trucks, H. B. Schlegel, P. M. W. Gill, B. G. Johnson, M. A. Robb, J. R. Cheeseman, T. A. Keith, G. A. Petersson, J. A. Montgomery, K. Raghavachari, M. A. Al-Laham, V. G. Zakrzewski, J. V. Ortiz, J. B. Foresman, J. Cioslowski, B. B. Stefanov, A. Nanayakkara, M. Challacombe, C. Y. Peng, P. Y. Ayala, W. Chen, M. W. Wong, L. J. Andres, E. S. Replogle, R. Gomperts, R. L. Martin, D. J. Fox, J. S. Binkley, D. J. Defrees, J. Baker, J. P. Stewart, M. Head-Gordon, C. Gonzalez, and J. A. Pople, *GAUSSIAN-94 (Revision A.1)*, Gaussian Inc., Pittsburgh, PA, 1995.
30. W. R. Wadt and P. J. Hay, *J. Chem. Phys.*, **82**, 284 (1985).
31. M. J. S. Dewar, E. G. Zoelirsch, E. Healy, and J. J. P. Stewart, *J. Am. Chem. Soc.*, **107**, 3902 (1985).
32. J. J. P. Stewart, *J. Comput. Chem.*, **10**, 209, 221 (1985).
33. SPARTAN (Version 3.1), Wavefunction, Inc., 18401 Von Karman Ave., #370, Irvine, CA 92715, USA.
34. M. W. Chase, C. A. Davies, J. R. Downey, D. J. Frurip, R. A. McDonald, and A. N. Szverud, *JANAF Thermochemical Tables*, *J. Phys. Chem. Ref. Data*, **14**(suppl. 1), 1985.
35. H. F. Moffat, K. F. Jensen, and R. W. Carr, *J. Phys. Chem.*, **95**, 145 (1991).
36. R. Becerra and R. Walsh, *J. Phys. Chem.*, **91**, 5765 (1987).
37. R. Walsh and J. M. Wells, *J. Chem. Soc. Faraday Trans. I*, **72**, 1212 (1976).
38. J. A. Seetula, Y. Feng, D. Gutman, P. W. Seakins, and M. J. Pilling, *J. Phys. Chem.*, **95**, 1658 (1991).
39. J. B. Pedley and B. S. Ioseard, *CATCH Tables*, University of Sussex, 1972, 1976.
40. T. N. Bell, K. A. Perkins, and P. G. Perkins, *J. Chem. Soc. Faraday Trans. I*, **77**, 1779 (1981).
41. R. Walsh, *Acc. Chem. Res.*, **14**, 246 (1981).
42. H. Chen, M. Krasowski, and G. Fitzgerald, *J. Chem. Phys.*, **98**, 8710 (1993).
43. T. V. Russo, R. L. Martin, and P. J. Hay, *J. Chem. Phys.*, **99**, 17085 (1995).
44. C. van Wullen, *Int. J. Quantum Chem.*, **58**, 147 (1996).
45. L.-Q. Lee and P. L. Cao, *J. Phys. Condens. Matter*, **6**, 169 (1994).
46. C. Kittel, *Introduction to Solid State Physics*, 6th Ed., Wiley, New York, 1986.
47. S. Bashkin and J. O. Stoner, Jr., *Atomic Energy Levels and Grottrian Diagrams*, Vol. 1, North Holland, Amsterdam, 1975.